

# Computational Actinide Chemistry

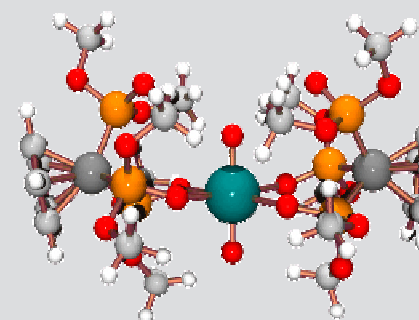
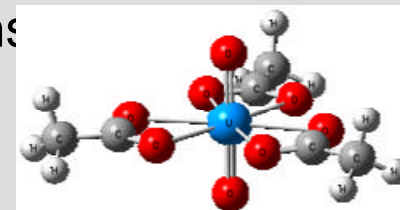
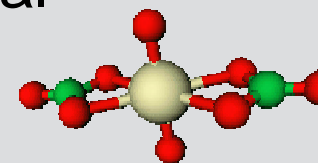
**Wibe A. de Jong**

**Environmental Molecular Sciences Laboratory**

**Pacific Northwest National Laboratory**

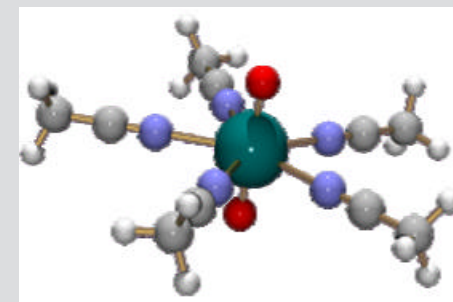
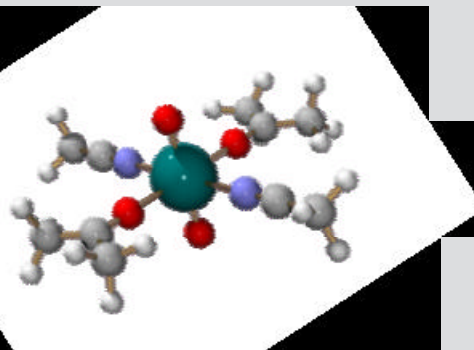
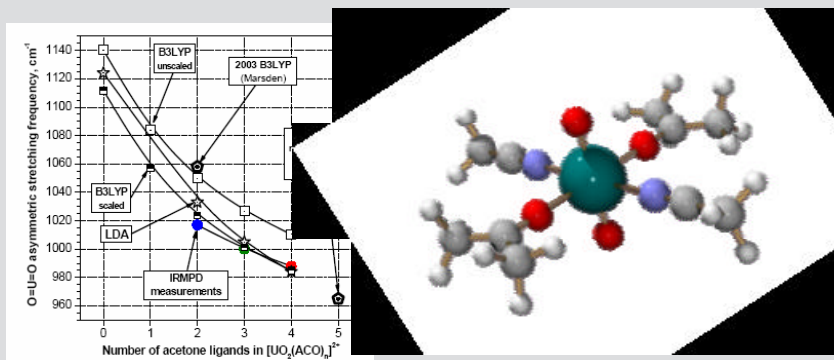
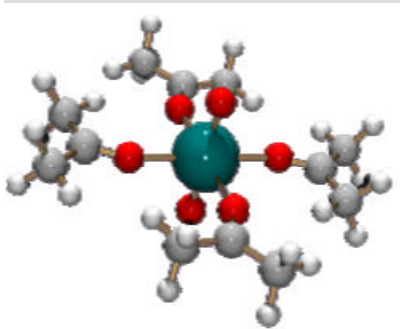
## Computational Actinide Chemistry at PNNL: Structures, vibrations and energetics

- ▶ Understanding actinide complex formation is vital
  - Hanford remediation efforts
  - Separations chemistry
  - Understanding basic properties of actinide systems
- ▶ Examples of complexes studied
  - Uranyl carbonates, nitrates, acetates, etc.
  - Klaui functionality, in collaboration with PNNL experimentalists
- ▶ Modeling results nowadays can be used for
  - Interpretation of experimental data
  - Guiding of experiment through prediction
  - Real interplay between theory and experiment!



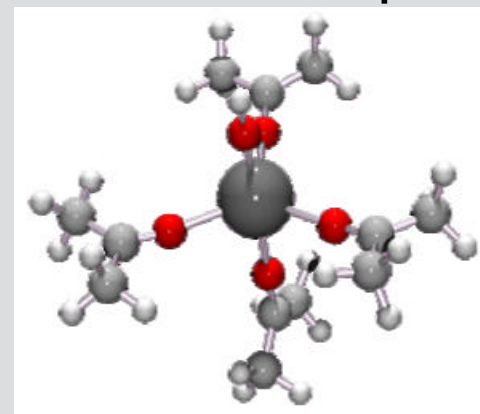
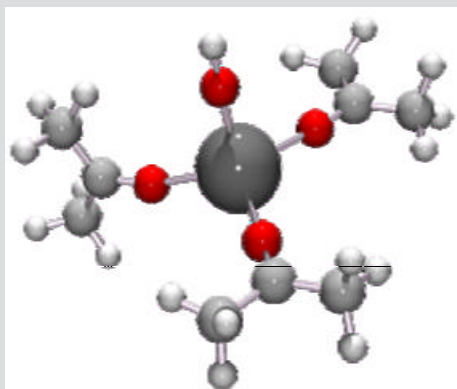
## Computational Actinide Chemistry at PNNL: INL collaboration gas phase spectroscopy (1)

- ▶ Uranyl acetates and acetonitriles (JACS in press)
  - Exciting experiments for computational actinide chemistry
  - Gas-phase: no environmental effects to worry about
  - Benchmark for computational methods
- ▶ Collaboration with experimentalists:
  - Groenewold, Gianotto, Cossel, *Idaho National Laboratory*
  - Van Stipdonk, *Wichita State University*
  - Oomens, Polfer, Moore, *FOM Instituut voor Plasmafysica*



## Computational Actinide Chemistry at PNNL: INL collaboration gas phase spectroscopy (2)

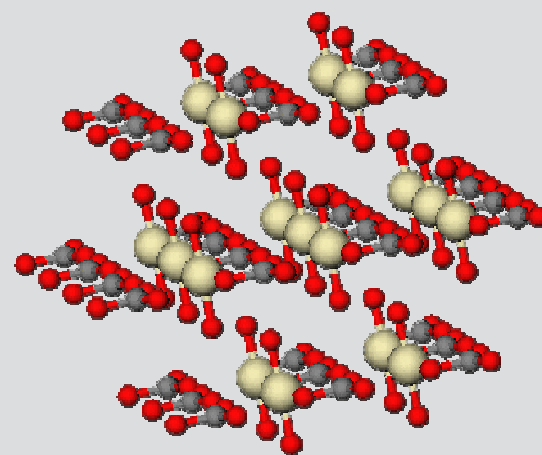
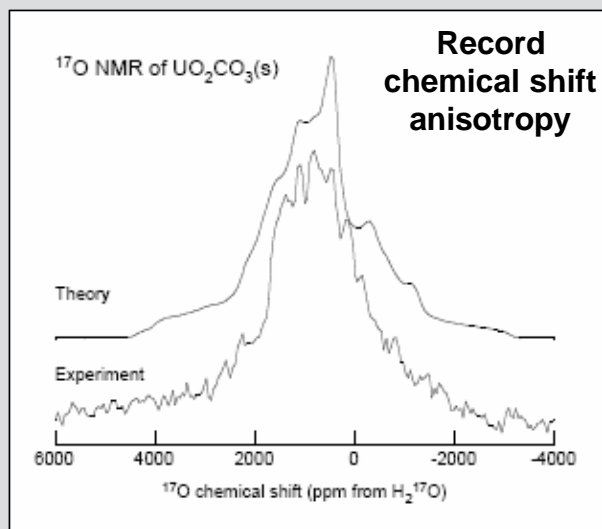
- ▶ FELIX-IR spectra measured for  $[\text{CeOH}]^{2+}$  bound to 3 and 4 acetones in gas-phase
- ▶ Open shell system with one 5f-orbital occupied



- ▶ Lots of photo fragmentation and weakly bound
- ▶ Very flat energy landscape with lots of local minima

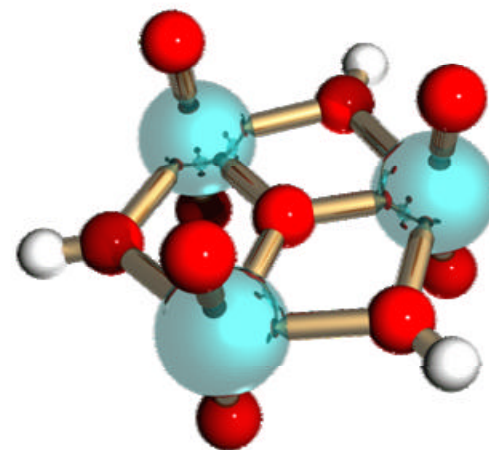
## Computational Actinide Chemistry at PNNL: NMR properties (1)

- ▶  $\text{UO}_2\text{CO}_3$  crystals:
  - Using NMR are sensitive probe of molecular environment (and speciation)
  - Experiments done at EMSL
  - Also working on other uranyl complexes

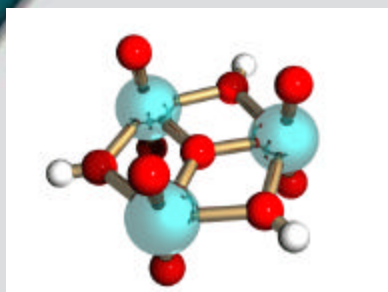


## Computational Actinide Chemistry at PNNL: NMR properties (2)

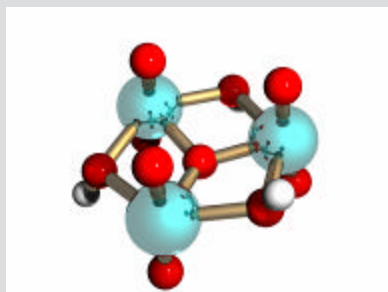
- ▶ Structure and NMR of  $[(\text{UO}_2)_3(\text{OH})_3]$
- ▶ Key compound in sol-gel processes relevant to nuclear fuel production
- ▶ Studied experimentally, NMR data unresolved
- ▶ Collaboration with Dave Dixon (Univ. Alabama)
- ▶ Modeling of free ion and ligands (HMTA) attached:
  - Structure
  - Vibration
  - NMR chemical shifts (central oxygen)



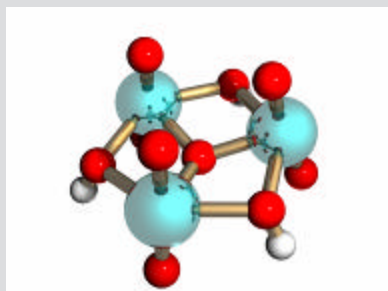
## $[(\text{UO}_2)_3(\text{OH})_3\text{O}]^+$ : some numbers...



- $D_{3H}$       9.35 kcal/mol
- Three imaginary frequencies
  - Isotropic shielding: -558 ppm

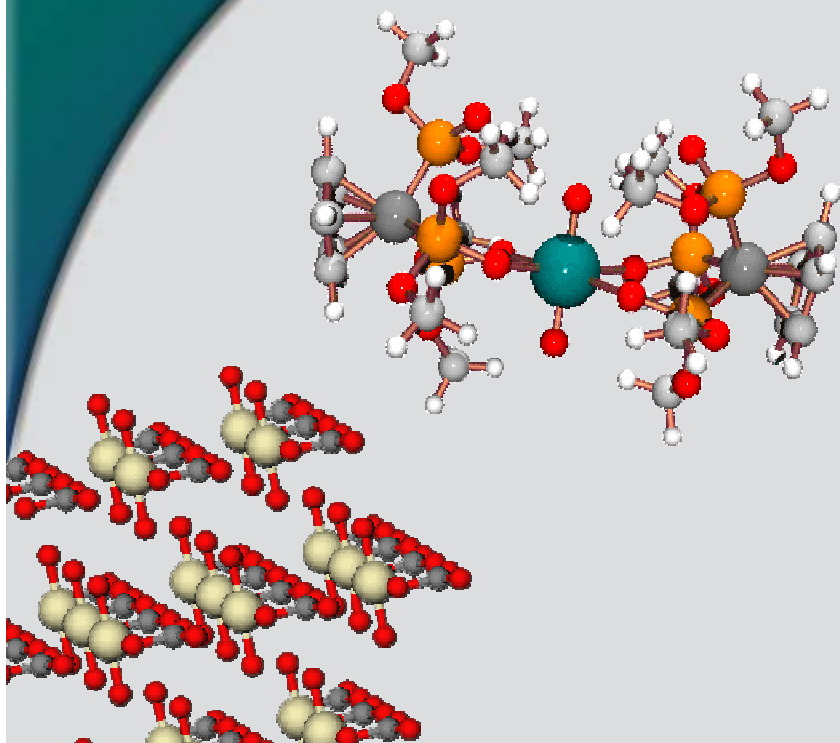


- $C_s$       1.94 kcal/mol
- No imaginary frequencies
  - Isotropic shielding: -648 ppm

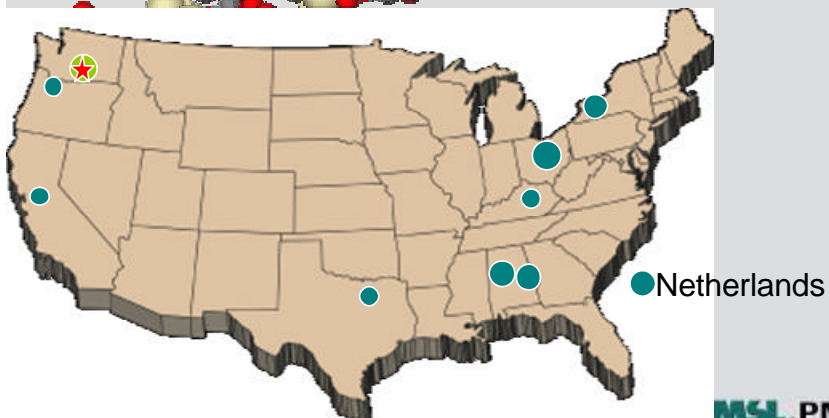


- $C_{3v}$       0.00 kcal/mol
- No imaginary frequencies
  - Isotropic shielding: -661 ppm

## Reliable Relativistic Quantum Chemistry Calculations for Molecules with Heavy Elements



- ▶ Modeling will contribute to the characterization of the interaction heavy elements with complexes present in nuclear waste tanks, soils, and ground water
- ▶ Inclusion of relativistic effects essential
- ▶ Results will provide interpretation and guidance for experimental research



### Grand Challenge PI: Wibe de Jong

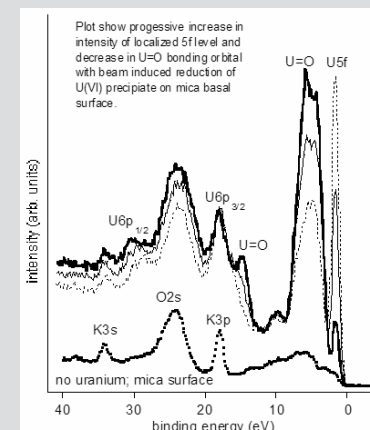
Distinguished users: Michael McKee, Jun Li, David Dixon

24 users on Grand Challenge project on MSCF resource at EMSL PNNL

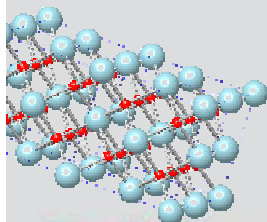
800,000 CPU Hours / year allocated

# Interfacial Molecular Chemistry at PNNL

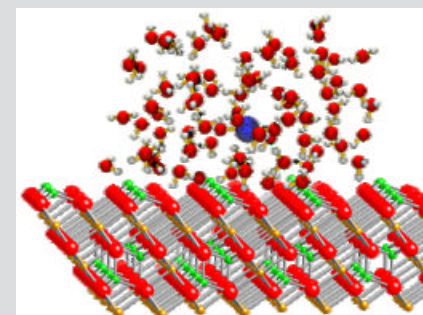
- ▶ Historically strong in research on interactions at interfaces
  - Biogeochemistry Grand Challenge (microbe/mineral interface)
  - Biological Grand Challenge (membranes)
  - Molecular Geochemistry
  - Catalysis Science
  - Hydrogen economy initiative
  - Aerosol surface chemistry



- ▶ Expanding in actinide chemistry at interfaces
  - Physical Sciences Building (wing for interfacial processes)
  - Future EMSL Radiochemistry Annex
  - BES funding (295K) for actinides at interfaces
  - Various interfaces
    - Actinides in solution interacting with metal-oxides
    - Actinide oxide phases



Battelle



## Getting the fastest time-to-solution: Hardware needs

- ▶ Quantum chemistry methodology needs
  - Lots of memory and disk (Otherwise lots of expensive recomputing)
    - Low latency and high bandwidth, asynchronous access
  - Very fast interconnect in order to scale quantum chemistry codes
  - Fast CPU is a given...
  
- ▶ Example of balanced architecture for chemistry is MSCF supercomputer at EMSL
  - 1,976-processor system, 11.8 Teraflop peak
  - 3-4 Gbyte memory/processor
  - 500 Terabytes of disk
  - Quadrics Interconnect
  
- 2005 **Greenbook**: More memory/processor needed!



## Getting the fastest time-to-solution: Software needs

- ▶ Quantum chemistry software needs to scale to 1000's and possibly 10,000's of processors

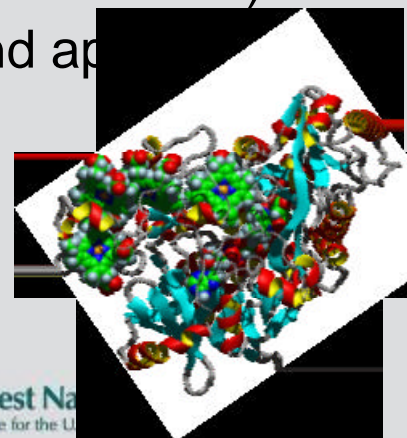
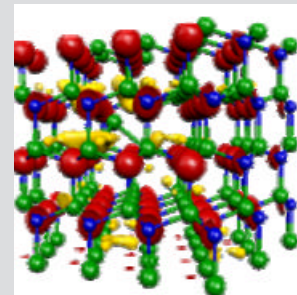


- Developed at EMSL/PNNL
- DOE's premier quantum chemistry code
- Highly scalable
  - Demonstrated running 1840 processors on EMSL machine
  - 62% efficiency on 11 TFlops for 37 hours (sections at 84%)



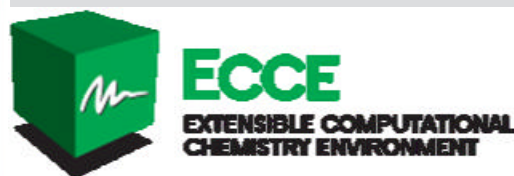
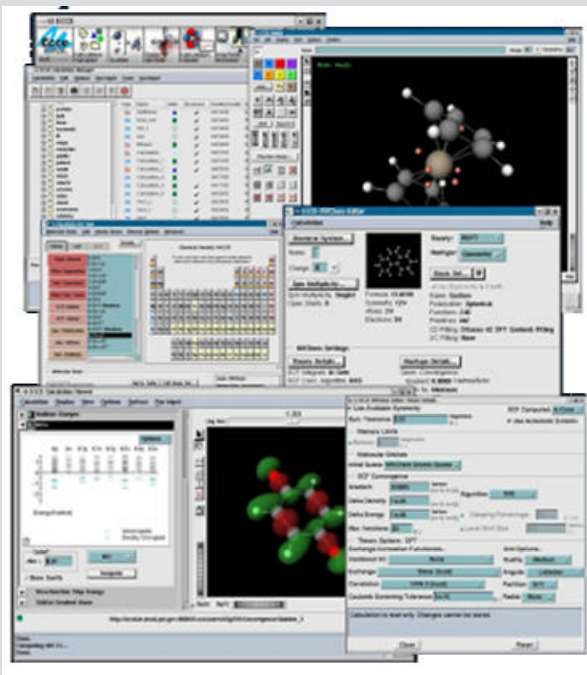
- Uses
  - To address global memory (i.e., on all processors)
  - Utilizes fastest API to communicate over network
  - Parallel math libraries

- ▶ Provides major modeling and simulation capability for molecular science
  - Broad range of **molecules**, including **biomolecules**, **nanoparticles** and heavy elements
  - Electronic structure of molecules
  - Increasingly extensive **solid state** capability
  - Molecular dynamics, molecular mechanics
- ▶ New software developments to model complex interfaces
  - Both Gaussian and Plane Wave based
  - Including relativistic effects (exact exchange for Plane Wave)
  - BES Funding, starts in April, both development and ap
- ▶ New developments are user driven
  - Large user base and Greenbook

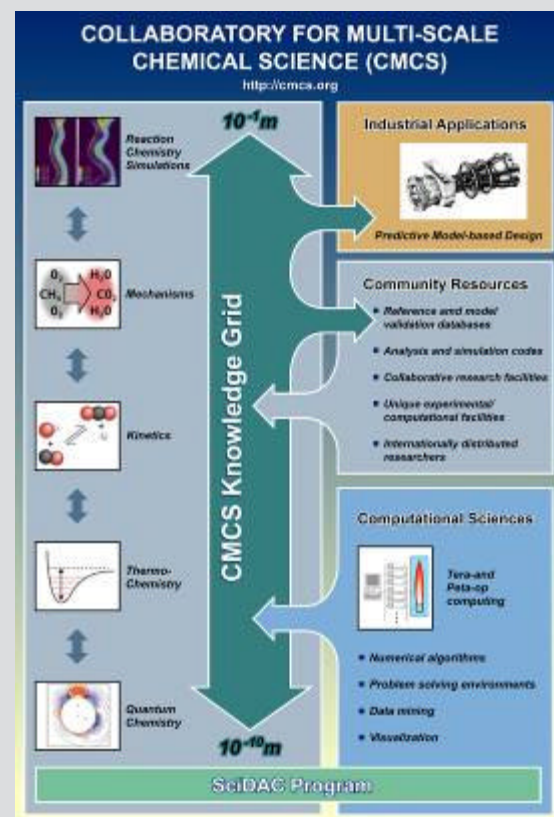


## End Stations need Visualization and Collaborative Tools

- ▶ Visualization tools provide new insights and interpretations
- ▶ Collaborative tools enable sharing of data within a science area and between science areas



- ▶ Both science enabling attributes



# CMCS Pilot Science Groups

- ▶ **DNS** – Jackie Chen, David Leahy
  - Feature detection & tracking in DNS data
- ▶ **HCCI University Consortium** – Bill Pitz
  - Homogeneous Charge Compression Ignition
- ▶ **PRIME** – led by Michael Frenklach
  - Development and publishing chemical reaction models
- ▶ **Real Fuels Project** – Wing Tsang, Tom Allison
  - Lead real fuels chemistry at NIST
- ▶ **IUPAC** – led by Branko Ruscic
  - Develop and publish validated thermochemical data
- ▶ **Quantum Chemistry** – Theresa Windus
  - QM Reference data

